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## Structural Characterization of Self-Assembled Monolayer Films of ( $\alpha$ -Quarterthiophene) phosphonate Bonded to the Silicon Native Oxide Surface

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*Electron transport across an interface might be controllable by chemically bonding monolayer films to a substrate surface; one possible application is in organic field effect transistors (OFETs), which necessitate a film that is dense and ordered.  $\alpha$ -Quarterthiophene-2-phosphonate (4TP) has a band gap comparable to  $\alpha$ -sexithiophene, which has been examined as a semiconducting layer in OFETs. A self-assembled monolayer (SAM) film of 4TP was grown on  $\text{SiO}_2/\text{Si}$ . Atomic force microscopy (AFM) showed a comprehensive film with no pinholes over large areas. Film thickness measurements were made by section analysis. An x-ray reflectivity study confirmed this measurement, which was calculated to be 1.8 nm, indicating that the 4TP units are nearly perpendicular to the surface. The profile for 4TP/ $\text{SiO}_2/\text{Si}$  is not as abrupt as that for clean  $\text{SiO}_2/\text{Si}$ , indicating some microscopic disorder within the 4TP film.*

Electron transport across or at interfaces might be controllable by chemically bonding monolayers to a substrate surface, which themselves could be modified to further enhance device function. One such possible application of surface-bound monolayers is for organic field effect transistors (OFETs), for use in "next generation" electronic devices. An interesting observation for OFETs is that most of the charge transport occurs through the first few electroactive organic monolayers. We were therefore interested in determining if such films might be prepared from phosphonate derivatives of oligoaromatic species via self assembly on the native oxide surface of silicon ( $\text{SiO}_2/\text{Si}$ ).  $\alpha$ -Quarterthiophene-2-phosphonate (4TP) would be an attractive example of an oligoaromatic phosphonate for use in such a film, since this material would be easy to process and quarterthiophene (4T) has a band gap comparable to  $\alpha$ -sexithiophene, which has been examined previously as a semiconducting layer in OFETs.

$\alpha$ -Quarterthiophene-2-phosphonic acid (4TPA) was prepared from 4T and was used to grow a self-as-

sembled monolayer (SAM) film on  $\text{SiO}_2/\text{Si}$  using our "T-BAG" (Tethering By Aggregation And Growth) method. Atomic force microscopy (AFM) showed a comprehensive monolayer on the surface (**Figure 1a**). The absence of pinholes in large ( $20\mu\text{m} \times 20\mu\text{m}$ , **Figure 1b**) sections revealed the high degree

of homogeneity in the SAM. Film thickness measurements therefore had to be made by section analysis (**Figure 1c**), based on the 4TP/ $\text{SiO}_2/\text{Si}$  film edge; this indicated the thickness to be  $2.0 \pm 0.2$  nm. Because the estimated length of 4TP is approximately 1.9 nm, this measurement suggests



Authors (from left, top): Eric L. Hanson and Jeffrey Schwartz; (from left, bottom): Norbert Koch and Mehmet Fatih Danisman; and (far right): Bert Nickel

only a small deviation, if any, of the 4TP moiety from vertical. The surface loading of the 4TP SAM was measured using quartz crystal microgravimetry (QCM) to be  $0.66 \pm 0.03$  nmol/cm<sup>2</sup>. This corresponds to a molecular cross-sectional area of  $25.1 \pm 0.4$  Å<sup>2</sup>/molecule, which is in the range reported for crystalline 4T ( $23.4$ - $25.6$  Å<sup>2</sup>/molecule).

An x-ray study was undertaken at the NSLS using beam line X10B (Exxon). Measurements were performed in reflectivity mode ( $v$ - $2v$ ), resulting in a momentum transfer,  $q_z$ , along the surface normal ( $q_z = 4\pi/\lambda \sin v$ ). Analyses of films of 4TP bonded to chemically reoxidized Si (HNO<sub>3</sub> oxidation of H-terminated Si; rms roughness 0.21 nm) were

performed in air, and both rinsed and unrinsed samples of 4TP/SiO<sub>2</sub>/Si were used. Data were analyzed using dynamical scattering theory. Various parameterizations for electron density profiles ( $n$ ) were used to model the reflectivity from the organic layer.

X-ray reflectivities were measured for 4TP/SiO<sub>2</sub>/Si after the film was prepared, thermally set on the surface (**Figure 2a**; O) (both before and after rinsing to remove any multiplayer material)(**Figure 2a**; ■), and were plotted against the momentum transfer,  $q_z$ . Intensities were multiplied by  $q^4$  to compensate for overall decay. As shown in **Figure 2a**, measurements made for the 4TP-covered surface before

rinsing show intensity variations in the range  $q_z \approx 0.1$  Å<sup>-1</sup>. These data indicate a structural feature in direct space on the order of about  $2\pi/0.1 = 70$  Å, indicative of multilayer formation. Reflectivity data from this multilayered structure could not be modeled. In contrast, reflectivity data obtained after rinsing (**Figure 2b**; ■) were well-modeled; the solid line in **Figure 2b** represents a best fit based on the inset electron density profile (normalized to the density of SiO<sub>2</sub>). The striped area in this profile is due to the organic film, which is calculated to be 1.8 nm thick. Furthermore, the profile shape for 4TP/SiO<sub>2</sub>/Si indicates some microscopic disorder exists within the 4TP film.

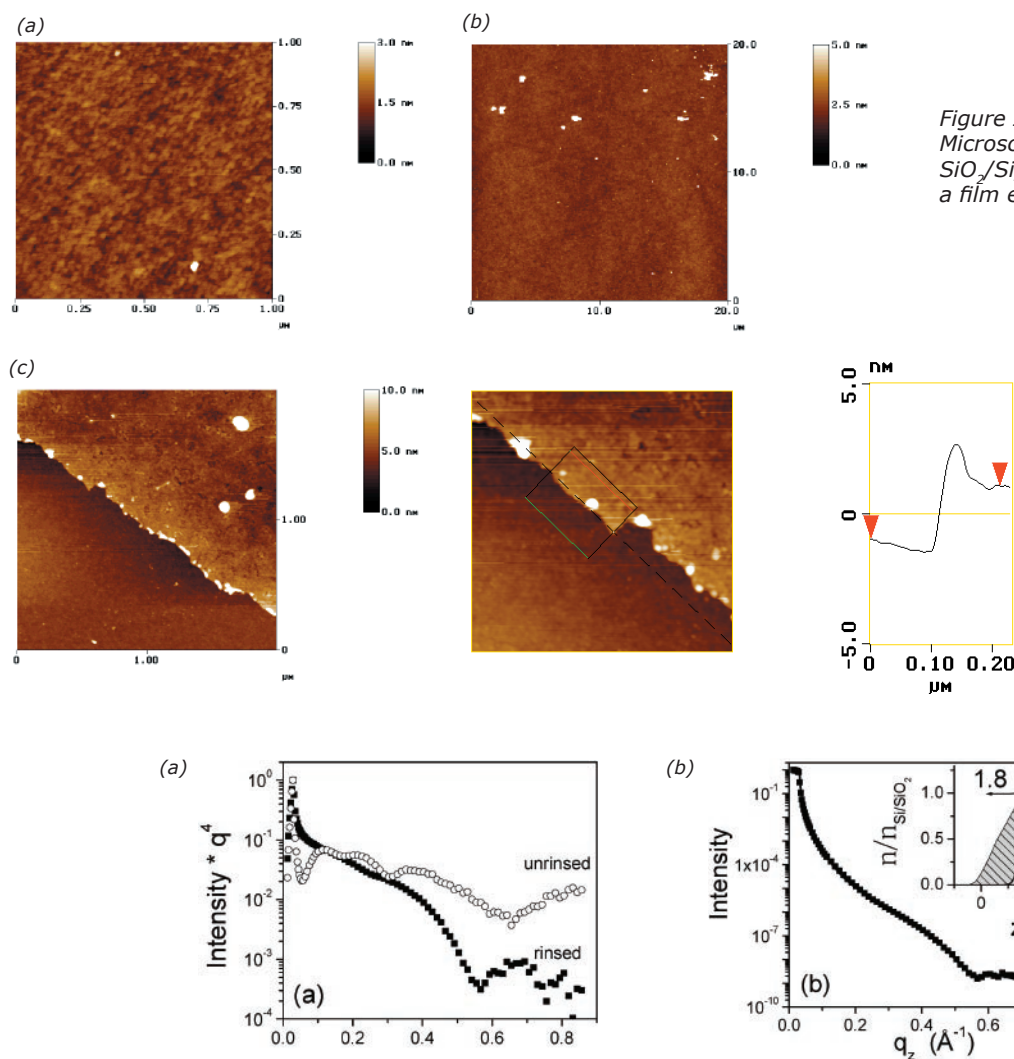


Figure 2. (a) X-ray reflectivity of unrinsed vs. rinsed 4TP/SiO<sub>2</sub>/Si and (b) profile of rinsed 4TP/SiO<sub>2</sub>/Si.